

MANGANESE VALENCE AND MINERAL SURFACE STRUCTURE DETERMINED WITH *IN SITU* SOFT X-RAY SPECTROSCOPY

Glenn Waychunas, David Shuh, and Mario Villalobos

Contact: Glenn Waychunas, 510/495-2224, gawaychunas@lbl.gov

RESEARCH OBJECTIVES

Manganese (Mn) minerals have high surface reactivity, redox potentials that can either reduce or oxidize adsorbed species, and high surface areas (fine grain sizes). These aspects make them extremely significant players in metal sequestration due to strong sorption and alteration in valence states (and hence solubility products) of solution species. Our goals are to determine how much information about Mn valence states and surface structure (i.e., surface mineral phase) can be extracted from K-edge oxygen and L-edge manganese x-ray fluorescence spectra, measured at the Advanced Light Source (ALS) at Berkeley Lab.

APPROACH

Experiments are designed to investigate both dry ultra-high-vacuum (UHV) mineral surfaces and surfaces in equilibrium with ambient water pressures. Fifteen different Mn mineral samples (both synthetic and natural) were examined at ALS Beam Line 9.3.2, using both photon yield and photoelectron yield, allowing simultaneous analysis of bulk and surface (5 nm) chemistry and structure.

ACCOMPLISHMENTS

Some representative spectra from our work are shown in Figure 1. Each valence state of Mn has well-defined features on the L-edge as well as a progressive shift in edge position. Accurate measurement (to about 1% relative) of valence ratios are possible for these models when two valence states are present. All phases showed the same bulk and surface valences, except for manganite (nominally Mn^{3+} with composition $MnOOH$), which has an oxidized surface.

The structure of the Mn phase has less effect on the Mn L spectra than it does on the O K-edge spectra. This is because the Mn L-edge transitions are mainly crystal field transitions, while the O K-edge transitions include multiple scattering, extended x-ray absorption fine structure (EXAFS), and valence-shell bound state features. This allows the two types of spectra, which can be collected in the same spectroscopy scans, to be used complementarily. For example, the manganite surface coating, less than 5 nm thick, appears to be mainly ramsdellite-like.

SIGNIFICANCE OF FINDINGS

These spectroscopy tools can be used to determine the precise chemical reactions at Mn mineral surfaces and whether redox reactions are occurring. Redox reactions can alter the

solubility and thus transportability of any surface-sorbed contaminant. In many waste situations, for example at Yucca Mountain, Nevada, small amounts of Mn phases can have large effects on contaminant sequestration. Hence, this type of analysis is crucial to a complete understanding of the ultimate fate of contaminants in Mn mineral-containing environments.

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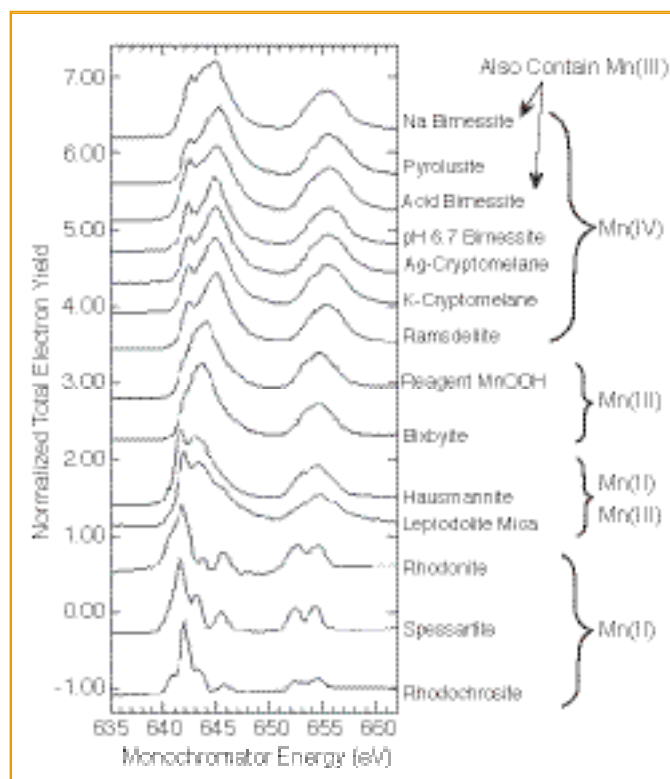


Figure 1. Mn L-edge fluorescence spectra for Mn minerals with different structures and valences. The differences in the Mn (II) spectra result from the varied coordination environments of Mn in each mineral (rhodochrosite—6 coordinated; spessartite—8 coordinated; rhodonite—5 and 6 coordinated). Both features and energy positions are characteristic of the Mn valence state.